Equation of state of a multicomponent d-dimensional hard-sphere fluid

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A simple recipe to derive the compressibility factor of a multicomponent mixture of d-dimensional additive hard spheres in terms of that of the one-component system is proposed. The recipe is based (i) on an exact condition that has to be satisfied in the special limit where one of the components corresponds to point particles; and (ii) on the form of the radial distribution functions at contact as obtained from the Percus-Yevick equation in the three-dimensional system. The proposal is examined for hard discs and hard spheres by comparison with well-known equations of state for these systems and with simulation data. In the special case of $d=3$, our extension to mixtures of the Carnahan-Starling equation of state yields a better agreement with simulation than the already accurate Boublík-Mansoori-Carnahan-Starling-Leland equation of state.

Due to their importance in liquid state theory, for years researchers have proposed empirical or semi-empirical (analytical) equations of state of various degrees of complexity for one-component hard-sphere fluids. Notable among these, is the celebrated Carnahan-Starling (CS) equation of state [1], which is not only rather simple but also accurate in comparison with computer simulation data. In the case of hard-sphere mixtures, the proposals, also empirical or semi-empirical in nature, are much more limited, with the Boublík-Mansoori-Carnahan-Starling-Leland (BMCSL) equation [2] standing out as the usual favorite. The situation for one-component hard-disc fluids is rather similar. Here, no analog of the CS equation using the $\frac{1}{3}(\mathrm{v})+\frac{2}{3}(\mathrm{c})$ recipe has been derived, due to the absence of an analytical solution of the Percus-Yevick (PY) equation in this instance. Nevertheless, accurate and simple equations of state have been proposed, such as the popular Henderson equation [3] and the recent one by the present authors [4]. Hard-disc mixtures, on the other hand, have received much less attention and the proposed equations of state for these systems are rather scarce. Given this scenario, the major aim of this paper is to show that, on the basis of a simple recipe, accurate equations of state of a multicomponent d-dimensional additive hard-sphere mixture may be derived, requiring the equation of state of the one-component system as the only input. The recipe makes use of a consistency condition that arises in the case that one of the components in the mixture has a vanishing size, as well as from some insight gained from the form of the radial distribution functions at contact given by the solution of the Percus-Yevick equation for a hard-sphere fluid in three dimensions [5].

Let us consider an N-component system of hard spheres in d dimensions. The total number density is ρ, the set of molar fractions is $\{x_1,\ldots,x_N\}$, and the set of diameters is $\{\sigma_1,\ldots,\sigma_N\}$. The volume packing fraction is $\eta=v_d\rho\langle\sigma^d\rangle$, where $v_d=(\pi/4)^{d/2}/\Gamma(1+d/2)$ is the volume of a d-dimensional sphere of unit diameter and $\langle\sigma^n\rangle\equiv\sum_i x_i\sigma_i^n$. In the case of a polydisperse mixture ($N\to\infty$) characterized by a size distribution $f(\sigma)$, $\langle\sigma^n\rangle\equiv\int d\sigma\sigma^n f(\sigma)$. Our goal is to propose a *simple* equation of state (EOS) for the mixture, $Z^{(N)}(\eta)$, consistent with a given EOS for a one-component system, $Z^{(1)}(\eta)$, where $Z=p/\rho k_BT$ is the usual compressibility factor. A consistency condition appears when one of the species, say the N-th, has a vanishing diameter, i.e. $\sigma_N\to 0$. In that case,

$$Z^{(N)}(\eta)\to(1-x_N)Z^{(N-1)}(\eta)+\frac{x_N}{1-\eta}. \tag{1}$$

At a more fundamental level, we will consider the contact values of the radial distribution functions, $g_{ij}^{(N)}(\sigma_{ij})$, the knowledge of which implies that of the EOS through the relation

$$Z^{(N)}(\eta)=1+2^{d-1}\eta\sum_{i=1}^N\sum_{j=1}^N x_ix_j\frac{\sigma_{ij}^d}{\langle\sigma^d\rangle}g_{ij}^{(N)}(\sigma_{ij}). \tag{2}$$

Taking as a guide the form of $g_{ij}^{(N)}$ obtained through the solution of the PY equation for hard spheres ($d=3$) [5], we propose to approximate $g_{ij}^{(N)}$ by a linear interpolation between $g^{(1)}$ and $(1-\eta)^{-1}$, namely

$$g_{ij}^{(N)}(\sigma_{ij})=\frac{1}{1-\eta}+\left[g^{(1)}(\sigma)-\frac{1}{1-\eta}\right]\frac{\langle\sigma^{d-1}\rangle}{\langle\sigma^d\rangle}\frac{\sigma_i\sigma_j}{\sigma_{ij}}. \tag{3}$$

When the above ansatz is inserted into equation (2), one gets

$$\begin{aligned}Z^{(N)}(\eta)-1 &= \left[Z^{(1)}(\eta)-1\right]2^{1-d}\Delta_0\\ &\quad+\frac{\eta}{1-\eta}\left(1-\Delta_0+\frac{1}{2}\Delta_1\right),\end{aligned} \tag{4}$$

where

$$\Delta_p = \frac{\langle\sigma^{d+p-1}\rangle}{\langle\sigma^d\rangle^2}\sum_{n=p}^{d-1}\frac{(d+p-1)!}{n!(d+p-1-n)!}\langle\sigma^{n-p+1}\rangle\langle\sigma^{d-n}\rangle,\quad (p=0,1). \tag{5}$$

This form of the EOS complies with the requirement (1). Note that equation (4) expresses $Z^{(N)}(\eta)-1$ as a linear combination of $Z^{(1)}(\eta)-1$ and $(1-\eta)^{-1}-1$, but the dependence of the coefficients on the size distribution is much more involved than in equation (3). The key outcome of this paper is the EOS given by equation (4), in which the compressibility factor of the mixture is obtained from that of the one-component system for arbitrary values of the dimensionality d and the number of components N. It is worth noticing that in the one-dimensional case, equation (4) yields the *exact* result $Z^{(N)}(\eta)=Z^{(1)}(\eta)$.

As a straightforward application of equation (4), one can easily get $B_n^{(N)} = v_d^{n-1}\langle\sigma^d\rangle^{n-1}\left[2^{1-d}\Delta_0 b_n^{(1)}+1-\Delta_0+\frac{1}{2}\Delta_1\right]$, where the virial coefficients $B_n^{(N)}$ are defined by $Z^{(N)}(\eta) = 1+\sum_{n=2}^{\infty}B_n^{(N)}\rho^{n-1}$. and where $b_n^{(1)}$ are the reduced virial coefficients of the one-component system, i.e. $Z^{(1)}(\eta)=1+\sum_{n=2}^{\infty}b_n^{(1)}\eta^{n-1}$.

We will now focus on the case of hard discs ($d=2$). Equation (4) then becomes

$$Z^{(N)}(\eta)=Z^{(1)}(\eta)\frac{\langle\sigma\rangle^2}{\langle\sigma^2\rangle}+\frac{1}{1-\eta}\left(1-\frac{\langle\sigma\rangle^2}{\langle\sigma^2\rangle}\right). \qquad (6)$$

The relationship between $Z^{(N)}(\eta)$ and $Z^{(1)}(\eta)$ as given by equation (6) rests on a different rationale from that pertaining to another simple proposal, namely the Conformal Solution Theory (CST) [6, 7]. In this latter theory, the EOS reads $Z_{\rm CST}^{(N)}(\eta)=Z^{(1)}(\eta_{\rm eff})$ with $\eta_{\rm eff}=\frac{1}{2}\left(1+\langle\sigma\rangle^2/\langle\sigma^2\rangle\right)\eta$, but we note that this equation *does not* comply with the general requirement (1). If the one-component system is assumed to be described by the Scaled Particle Theory (SPT) [8], our extension to mixtures takes on a particularly simple form:

$$Z_{\rm SPT}^{(N)}(\eta)=\frac{1-\left(1-\langle\sigma\rangle^2/\langle\sigma^2\rangle\right)\eta}{(1-\eta)^2}. \qquad (7)$$

This is precisely the true SPT EOS for mixtures [7], which is indeed rewarding. The EOS $Z^{(1)}(\eta) = \left[1-2\eta+(2\eta_0-1)\eta^2/\eta_0^2\right]^{-1}$, where $\eta_0=\sqrt{3}\pi/6$ is the crystalline close-packing fraction, has been recently proposed by us [4] to describe a one-component system. When this EOS, hereafter referred to as the SHY EOS following the nomenclature introduced in reference [9], is substituted into equation (6), we obtain the following extension:

$$Z_{\rm eSHY}^{(N)}(\eta)=\frac{\langle\sigma\rangle^2/\langle\sigma^2\rangle}{1-2\eta+(2\eta_0-1)\eta^2/\eta_0^2}+\frac{1}{1-\eta}\left(1-\frac{\langle\sigma\rangle^2}{\langle\sigma^2\rangle}\right). \qquad (8)$$

The well-known Henderson (H) EOS [3] can also be extended:

$$Z_{\rm eH}^{(N)}(\eta)=\frac{1-\left(1-\langle\sigma\rangle^2/\langle\sigma^2\rangle\right)\eta+(b_3^{(1)}-3)\left(\langle\sigma\rangle^2/\langle\sigma^2\rangle\right)\eta^2}{(1-\eta)^2}, \qquad (9)$$

where $b_3^{(1)}=\frac{16}{3}-\frac{4}{\pi}\sqrt{3}$. This equation is quite similar to the one proposed by Barrat *et al.* [7], the only difference being that the coefficient of η^2 in the numerator is $b_3^{(N)}-1-2\langle\sigma\rangle^2/\langle\sigma^2\rangle$, where $b_3^{(N)}$ is the exact (reduced) third virial coefficient. Nevertheless, since $b_3^{(N)}$ is well approximated by $1+(b_3^{(1)}-1)\langle\sigma\rangle^2/\langle\sigma^2\rangle$, both EOS are practically indistinguishable. Although we could consider the extensions of other EOS originally proposed for a one-component system of hard discs (for a list of many such EOS we refer the reader to references [4, 9]), for the sake of simplicity we will restrict our analysis to the SPT, eSHY and eH EOS.

Let us now consider the virial coefficients $B_n^{(N)}$ for hard discs. It follows that in this case $B_n^{(N)} = (\pi/4)^{n-1}\langle\sigma^2\rangle^{n-1}\left[1+(b_n^{(1)}-1)\langle\sigma\rangle^2/\langle\sigma^2\rangle\right]$. This equation yields the exact second virial coefficient [7], the higher coefficients being approximate. In the particular case of a binary mixture, the composition-independent coefficients $B_{n_1,n_2}^{(2)}$ are defined through $B_n^{(2)}=\sum_{n_1=0}^{n}\frac{n!}{n_1!(n-n_1)!}B_{n_1,n-n_1}^{(2)}x_1^{n_1}x_2^{n-n_1}$. According to equation (6),

$$\begin{aligned}B_{n_1,n_2}^{(2)} &= \left(\frac{\pi}{4}\right)^{n-1}\sigma_1^{2(n-1)}\alpha^{2(n_2-1)}\left[\frac{n_1}{n}\alpha^2+\frac{n_2}{n}+\left(b_n^{(1)}-1\right)\right.\\ &\left.\times\left(\frac{n_1(n_1-1)}{n(n-1)}\alpha^2+\frac{2n_1n_2}{n(n-1)}\alpha+\frac{n_2(n_2-1)}{n(n-1)}\right)\right], \end{aligned} \qquad (10)$$

where $n=n_1+n_2$ and $\alpha=\sigma_2/\sigma_1$. This form has the same structure as the interpolation formula suggested by Wheatley [10]. In fact, he proposes an EOS (henceforth labelled as W) of the form

$$Z_{\rm W}^{(2)}(\eta)=\frac{\sum_{n=0}^{7}c_n\eta^n}{(\eta-\eta_0)^2}, \qquad (11)$$

where the coefficients c_n are chosen so as to reproduce the first eight virial coefficients given by the interpolation formula [10].

Now, let us consider the case $d=3$. Equation (4) then yields

$$\begin{aligned}Z^{(N)}(\eta) &= =1+\left[Z^{(1)}(\eta)-1\right]\frac{\langle\sigma^2\rangle}{2\langle\sigma^3\rangle^2}\left(\langle\sigma^2\rangle^2+\langle\sigma\rangle\langle\sigma^3\rangle\right)\\ &+\frac{\eta}{1-\eta}\left[1-\frac{\langle\sigma^2\rangle}{\langle\sigma^3\rangle^2}\left(2\langle\sigma^2\rangle^2-\langle\sigma\rangle\langle\sigma^3\rangle\right)\right]. \end{aligned} \qquad (12)$$

Using the CS EOS [1], $Z^{(1)}(\eta)=(1+\eta+\eta^2-\eta^3)/(1-\eta)^3$, the result may be expressed as

$$Z_{\rm eCS}^{(N)}(\eta)=Z_{\rm BMCSL}^{(N)}(\eta)+\frac{\eta^3}{(1-\eta)^3}\frac{\langle\sigma^2\rangle}{\langle\sigma^3\rangle^2}\left(\langle\sigma\rangle\langle\sigma^3\rangle-\langle\sigma^2\rangle^2\right), \qquad (13)$$

where the BMCSL EOS [2] is

$$Z_{\rm BMCSL}^{(N)}(\eta)=\frac{1}{1-\eta}+\frac{3\eta}{(1-\eta)^2}\frac{\langle\sigma\rangle\langle\sigma^2\rangle}{\langle\sigma^3\rangle}+\frac{\eta^2(3-\eta)}{(1-\eta)^3}\frac{\langle\sigma^2\rangle^3}{\langle\sigma^3\rangle^2}. \qquad (14)$$

As another, example, let us consider the Carnahan-Starling-Kolafa (CSK) EOS [11], $Z^{(1)}(\eta) = [1 + \eta + \eta^2 - 2\eta^3(1 + \eta)/3]/(1 - \eta)^3$. Its extension is

$$Z^{(N)}_{\mathrm{eCSK}}(\eta) = Z^{(N)}_{\mathrm{eCS}}(\eta) + \frac{\eta^3(1-2\eta)}{(1-\eta)^3} \frac{\langle\sigma^2\rangle}{6\langle\sigma^3\rangle^2} \times \left(\langle\sigma^2\rangle^2 + \langle\sigma\rangle\langle\sigma^3\rangle\right), \qquad (15)$$

which does not coincide with Boublík's extension to mixtures of the CSK EOS [12]:

$$Z^{(N)}_{\mathrm{BCSK}}(\eta) = Z^{(N)}_{\mathrm{BMCSL}}(\eta) + \frac{\eta^3(1-2\eta)}{(1-\eta)^3} \frac{\langle\sigma^2\rangle^3}{3\langle\sigma^3\rangle^2}. \qquad (16)$$

Recently, Henderson and Chan (HC) have proposed a modification of the BMCSL EOS [13, 14] for the *particular* case of a binary mixture in which the concentration of the large spheres is exceedingly small, starting from an *asymmetric* prescription for the radial distribution functions at contact. The resulting EOS, with $\sigma_1 \geq \sigma_2$, is

$$\begin{aligned} Z^{(2)}_{\mathrm{HC}}(\eta) = {} & Z^{(2)}_{\mathrm{BMCSL}}(\eta) + \frac{4\eta x_1}{\langle\sigma^3\rangle} \left\{ x_1\sigma_1^3 \left\{ \frac{3\eta}{2(1-\eta)^2} \right.\right. \\ & \left(1 - \frac{\langle\sigma^2\rangle}{\langle\sigma^3\rangle}\sigma_1\right) + \frac{\eta^2}{2(1-\eta)^3}\left[1 - \left(\frac{\langle\sigma^2\rangle}{\langle\sigma^3\rangle}\sigma_1\right)^2\right] \\ & \left. + \exp\left[\frac{3\eta}{2(1-\eta)^2}\left(\frac{\langle\sigma^2\rangle}{\langle\sigma^3\rangle}\sigma_1 - 1\right)\right] - 1 \right\} \\ & + \frac{\eta^2 x_2}{4(1-\eta)^3}\left(\frac{\langle\sigma^2\rangle}{\langle\sigma^3\rangle}\sigma_2\right)^2 (\sigma_1 - \sigma_2) \\ & \left. \times \left[(\sigma_1+\sigma_2)^2 - \eta\sigma_2(\sigma_1^2 + \sigma_2^2 + \sigma_1\sigma_2)\frac{\langle\sigma^2\rangle}{\langle\sigma^3\rangle}\right]\right\}. \end{aligned} \qquad (17)$$

We shall now perform a comparison with the (very few) available computer simulation data. We begin with hard-disc mixtures. In figure 1 we display the packing-fraction dependence of the compressibility factor Z for the SPT, W, eH and eSHY EOS, together with the simulation results of Barrat *et al.* [7], for the binary mixture defined by $x_1 = 0.351$ and $\sigma_2/\sigma_1 = 0.8$. In this case, the performance of the eSHY EOS is outstanding and clearly superior to all the other choices. To complete the picture, in figure 2 we present the results for the ratio of the fifth virial coefficient to the fourth power of the (exact) second virial coefficient as a function of the larger disc concentration and for two size ratios. Here, the best agreement with the numerical data of Wheatley [15] is obtained with the eH EOS, which is not very surprising since in the one-component case ($x_1 = 1$) it gives a very good estimate of this ratio. Nevertheless, the overall trends including the position of the maximum are still captured in all approximations.

As far as hard-sphere mixtures are concerned, the following comments can be made. To our knowledge, only simulation results for binary mixtures have been reported. The most recent data [16] indicate that the

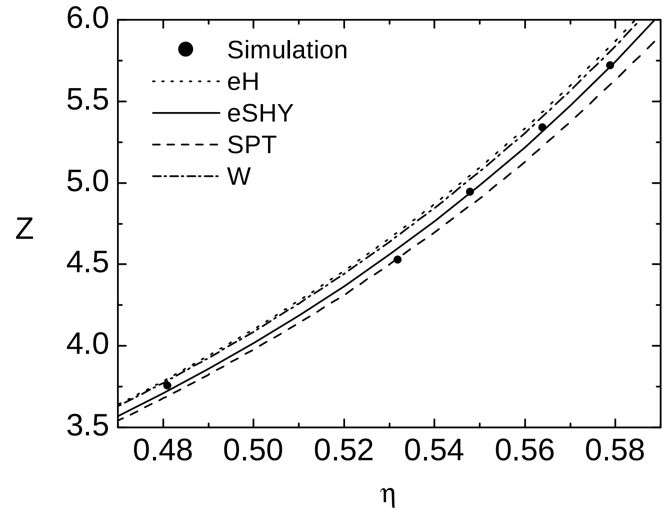

FIG. 1: Compressibility factor as a function of the packing fraction for a binary mixture of hard discs defined by $x_1 = 0.351$ and $\sigma_2/\sigma_1 = 0.8$.

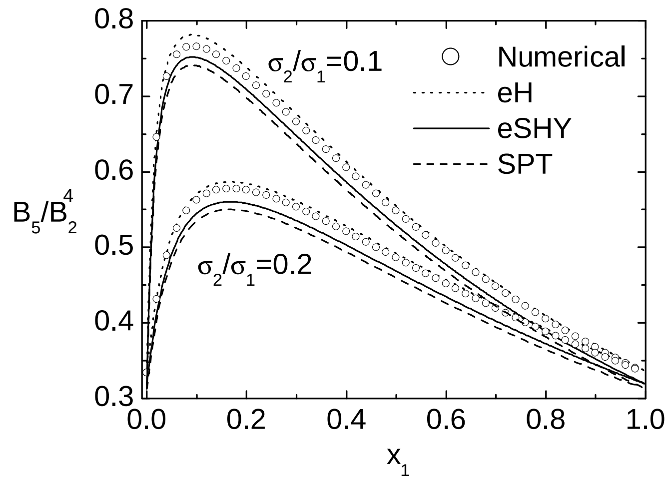

FIG. 2: Fifth virial coefficient as a function of x_1 for two binary mixtures of hard discs defined by $\sigma_2/\sigma_1 = 0.1$ and $\sigma_2/\sigma_1 = 0.2$.

BMCSL EOS underestimates the pressure as obtained through simulation. In fact, the BCSK EOS is geared to correct this deficiency, at least for $\eta < 0.5$, in a similar fashion as the CSK EOS corrects the CS EOS. As a general trend, for $\eta < 0.5$, our extended EOS, namely the eCS and the eCSK, also go in the correct direction. Moreover, in this density range, $Z_{\mathrm{BMCSL}} < Z_{\mathrm{eCS}} < Z_{\mathrm{eCSK}}$ and $Z_{\mathrm{BMCSL}} < Z_{\mathrm{BCSK}} < Z_{\mathrm{eCSK}}$. Although limited in scope, the results shown in figure 3 illustrate these features. Here we have considered an equimolar binary mixture with size ratio $\sigma_2/\sigma_1 = 0.6$. As the differences between the values predicted by the various EOS for the compressibility factor Z are very small, we have chosen to present the results, including the simulation data of Yau *et al.* [14] (open circles) and Barošová *et al.* [16] (filled

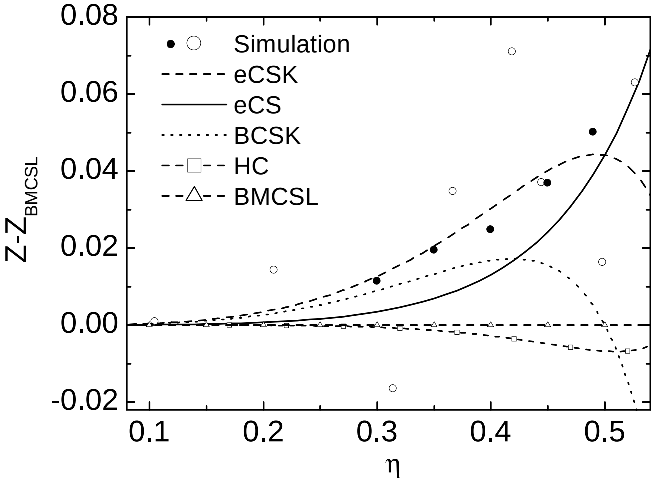

FIG. 3: Compressibility factor as a function of the packing fraction, relative to the BMCSL value, for an equimolar binary mixture of hard spheres with $\sigma_2/\sigma_1 = 0.6$.

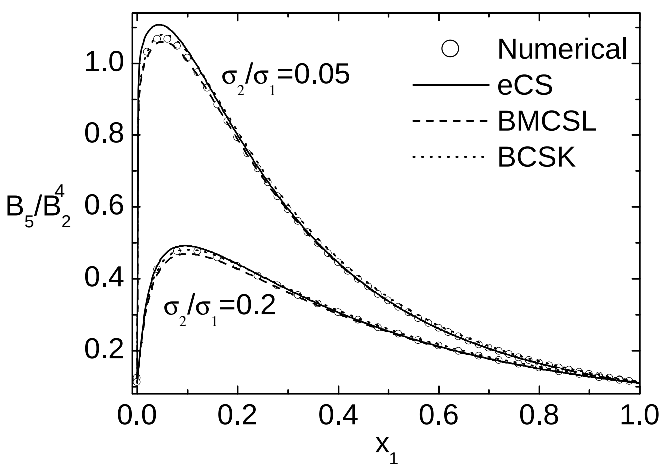

FIG. 4: Fifth virial coefficient as a function of x_1 for two binary mixtures of hard spheres defined by $\sigma_2/\sigma_1 = 0.05$ and $\sigma_2/\sigma_1 = 0.2$.

circles), in terms of the packing fraction dependence of $Z - Z_{\rm BMCSL}$. Despite the scatter of the simulation results of Yau *et al.* [14], it is apparent that, depending on the range, both the eCSK and eCS EOS seem to do a better job than either the BMCSL, BCSK or HC EOS (although in all fairness we should add that the equimolar condition is beyond the scope for which the latter EOS was originally devised). In fact, if one considers a higher density point computed by Yau *et al.* [14] ($\eta = 0.59$, $Z_{\rm simul} - Z_{\rm BMCSL} = 0.26$) that is off the scale, it appears that the overall trend is better captured by the eCS EOS, although for $\eta < 0.5$ the eCSK should probably be the preferred EOS. The results for the composition dependence of the fifth virial coefficient for a binary mixture and two values of σ_2/σ_1 displayed in figure 4 also indicate that all the approximations lead to very good values as compared to the recent numerical data of Enciso *et al.* [17], with a slight superiority of the BCSK EOS for the region around the maximum. The HC and the eCSK results have not been included, since they are almost identical to the ones of the BMCSL and the eCS, respectively.

In conclusion, it is fair to state that we have introduced a very simple and general recipe that allows one to get a reasonably accurate approximation to the EOS of a multicomponent mixture of d-dimensional hard-spheres from any reasonable EOS of the one-component system. It also seems that, as exemplified in the case of binary three-dimensional hard-sphere mixtures, the more accurate the EOS of the one-component system, the better results the approximation yields.

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